SINGLE BASE PROPELLANT DEGRADATION IN A COMMERCIAL BALL POWDER

Eric R. Bixon
Henry A. Grau
Dan J. Murphy

US ARMY ARDEC
Picatinny, NJ 07806

- Ball powder is commonly used in small caliber ammunition systems. It is generally stabilized with diphenylamine (DPA).
- Samples of the propellant have been subjected to accelerated aging at 50, 60, 70 and 80 °C.

- Analyzed using HPLC
- Concentrations of DPA and the daughter products determined

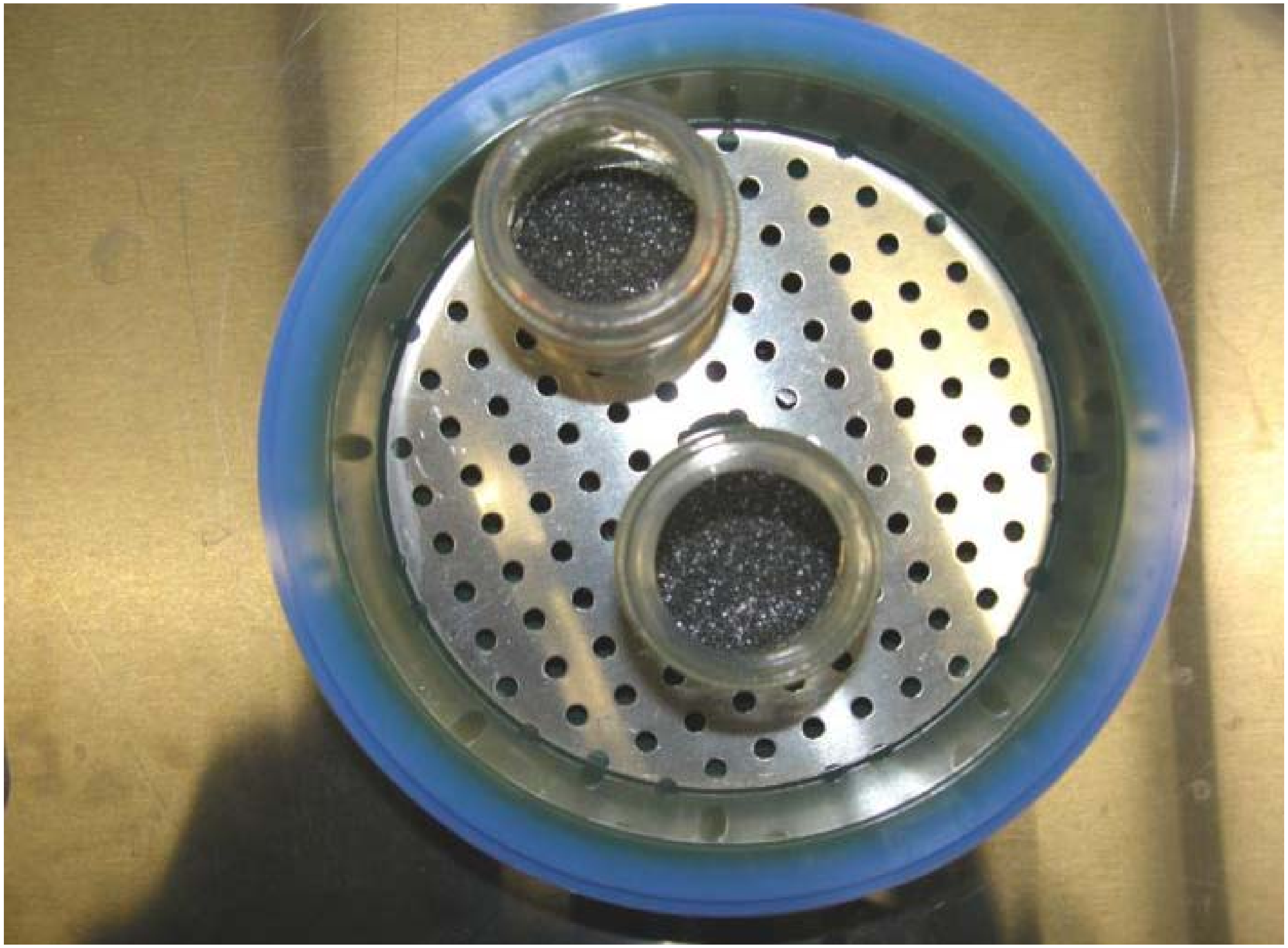


Figure 1.
Storage Configuration of Propellant in Desiccator

HUMIDITY LEVEL TEMPERATURE	STD	100 % RH
80 °C	X	X
70 °C	X	X
60 °C	X	X
50 °C	X	X

STD in Table I represents a desiccator without a humidity source

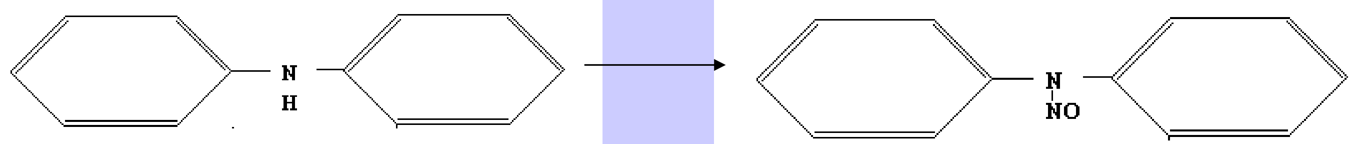
100 % RH represents a desiccator with water at the bottom

Nitrocellulose gives off decomposition products. In this paper they are referred to as NOx species. Autocatalytic decomposition of propellant occurs when NOx species remain inside the propellant grain. This is an exothermic process and unless the heat is removed at a sufficient rate to keep the grain temperature constant, the temperature of the grain will rise.

The level of stabilizer that has historically been chosen as the “safe” level for propellants is .2 weight percent DPA.

$$A \xrightarrow{k1} R$$

$$\text{DPA} \xrightarrow{k1} \text{N-NITROSO-DPA}$$



1st decomposition product is NNO-DPA

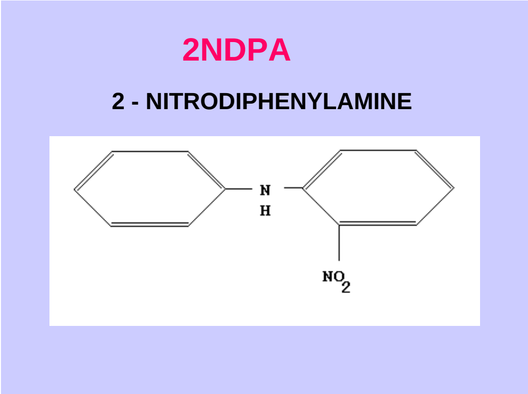


Figure 3. 2NDPA is one of the reaction products formed after the NNO DPA

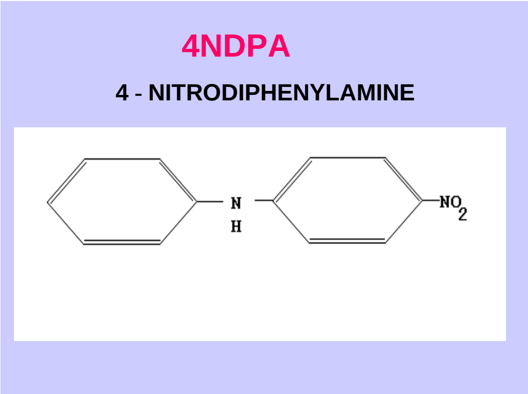


Figure 4. 4NDPA is the other reaction product formed after the NNO reacts

$$A \xrightarrow{k} S$$

$$\{NO_x\} = f(T)\, alone, \quad not\, t$$

$$-dC_A/dt = k_0 \times \{NO_x\}$$

$$k_{new} = k\{NO_x\}$$

$$-dC_A/dt = k_1 C_A \times \{NO_x\}$$

$$k = k_0 \exp\{-E_A / RT\}$$

$$-dC_A/dt = k_1 C_A{}^n \times \{NO_x\}$$

$$-dC_A/dt = \{k_1 + k_2 \times C_A\} \times \{NO_x\}$$

Reaction Kinetic Rate Expressions.

Reaction Kinetic Models.

$$A \xrightarrow{k} S$$

$$-dC_A / dt = k_0 \times \{NO_x\}$$

$$-dC_A / dt = k_1 C_A \times \{NO_x\}$$

$$-dC_A / dt = k_1 C_A{}^n \times \{NO_x\}$$

$$-dC_A / dt = \{k_1 + k_2 \times C_A\} \times \{NO_x\}$$

$$\{NO_x\} = f(T)\ alone, \quad not \quad t$$

$$k_{new} = k\{NO_x\}$$

$$k = k_0 \exp\{-E_A / RT\}$$

Table II. Initial values for diphenylamine (DPA) and Remaining Effective Stabilizer (RES)

Wt % DPA	Wt % RES
0.579	1.079
0.59	1.088
0.568	1.068
0.554	1.105
0.549	1.087

Table IV. Reaction Kinetic data at 50 C for DPA aged in the dry configuration

Table III. Reaction Kinetic data at 50 C for DPA

50 C Wet	
Wt % DPA	t(days)
0.446	14
0.429	28
0.38	42
0.35	60
0.12	120
0.15	150
0.047	150
0.04	300
0.05	330
0.04	360
0.05	390

50 C - Dry	
Wt % DPA	t(days)
0.485	14
0.479	28
0.47	42
0.47	60
0.41	120
0.36	150
0.21	300
0.19	330
0.18	360
0.16	390

Tables V and VI. Reaction Kinetic data at 50 C for RES

50 C - Dry	
t (days)	Wt. % RES
14	0.986
28	0.984
42	0.94
60	0.94
120	0.932
150	0.9
270	0.78
300	0.74
210	0.832
240	0.808
270	0.78
300	0.74
330	0.807
360	0.781
390	0.772

50 C Wet	
t(days)	Wt. % RES
14	1.007
28	0.981
42	0.94
60	0.93
120	0.96
150	0.929
150	0.918
180	0.886
210	0.863
240	0.851
270	0.74
300	0.76
330	0.752
360	0.749
390	0.745

Table VII. Hourly temperature variation for hot and humid temperature cycle as defined in AR 70-38

time	T in C	time	T in C
1:00	35	13:00	66
2:00	34	14:00	69
3:00	34	15:00	71
4:00	34	16:00	69
5:00	33	17:00	66
6:00	33	18:00	63
7:00	36	19:00	58
8:00	40	20:00	50
9:00	44	21:00	41
10:00	51	22:00	39
11:00	57	23:00	37
12:00	62	24:00	35

Figure 2. RES dry zero order

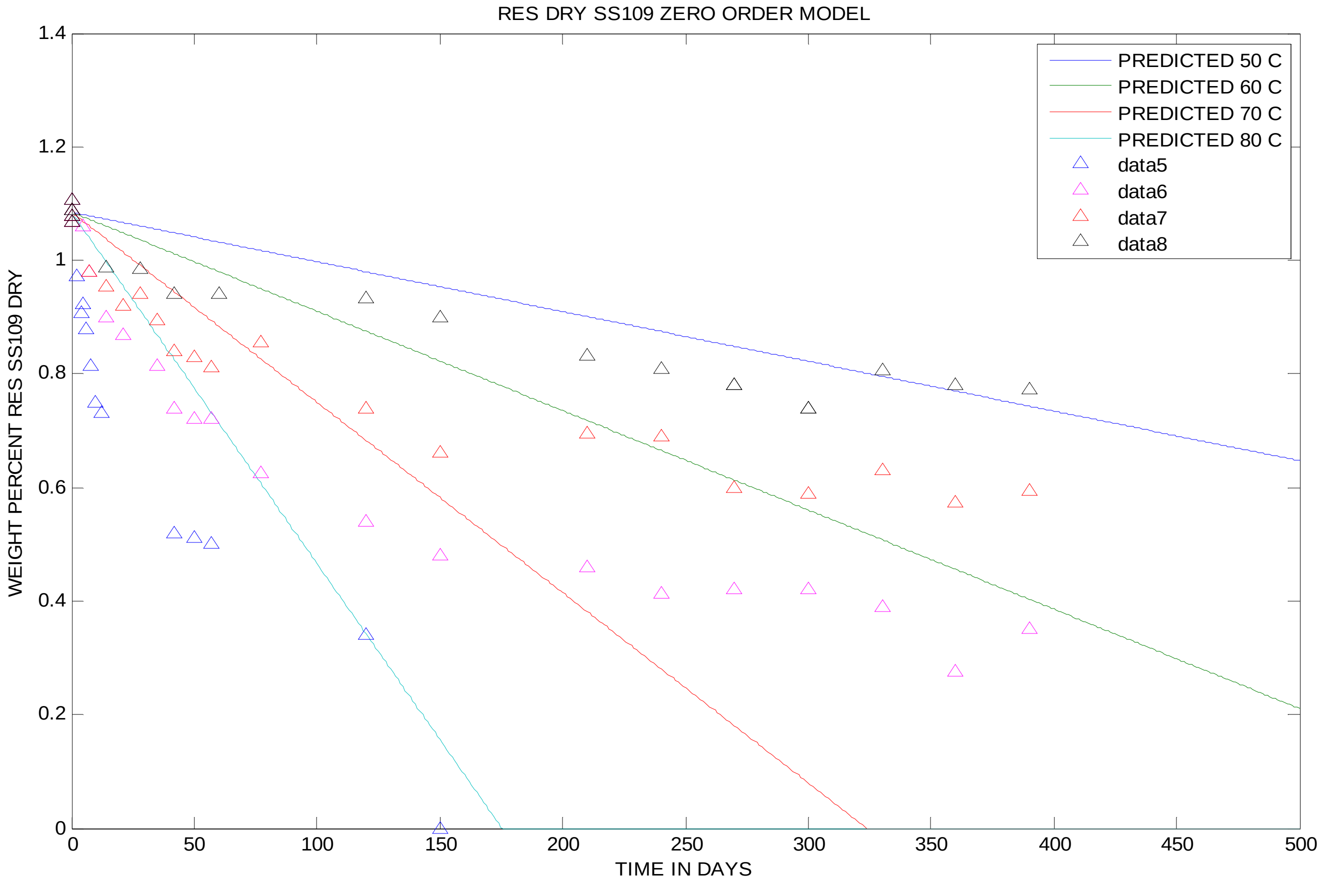


Figure 3. Res dry first order

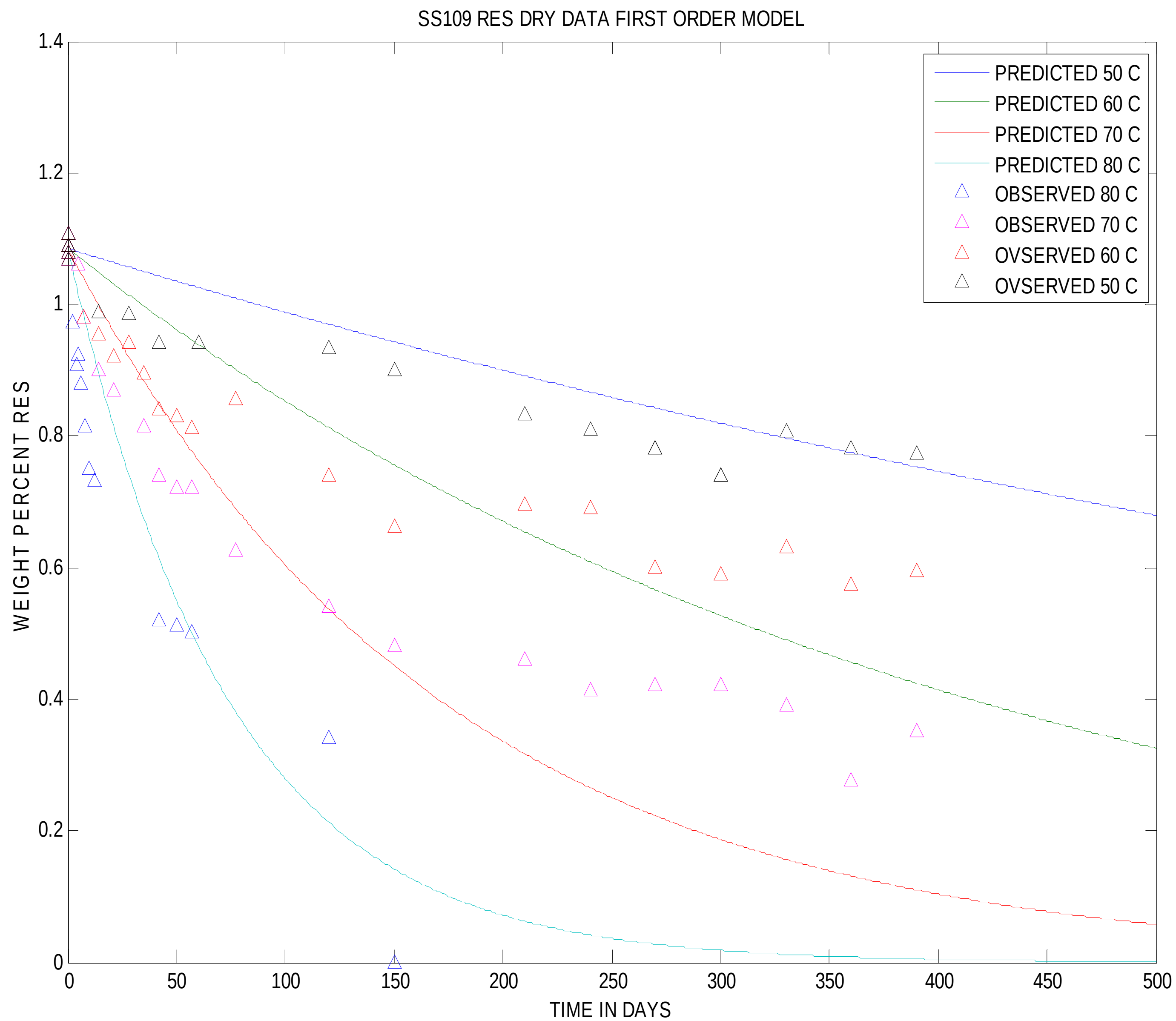
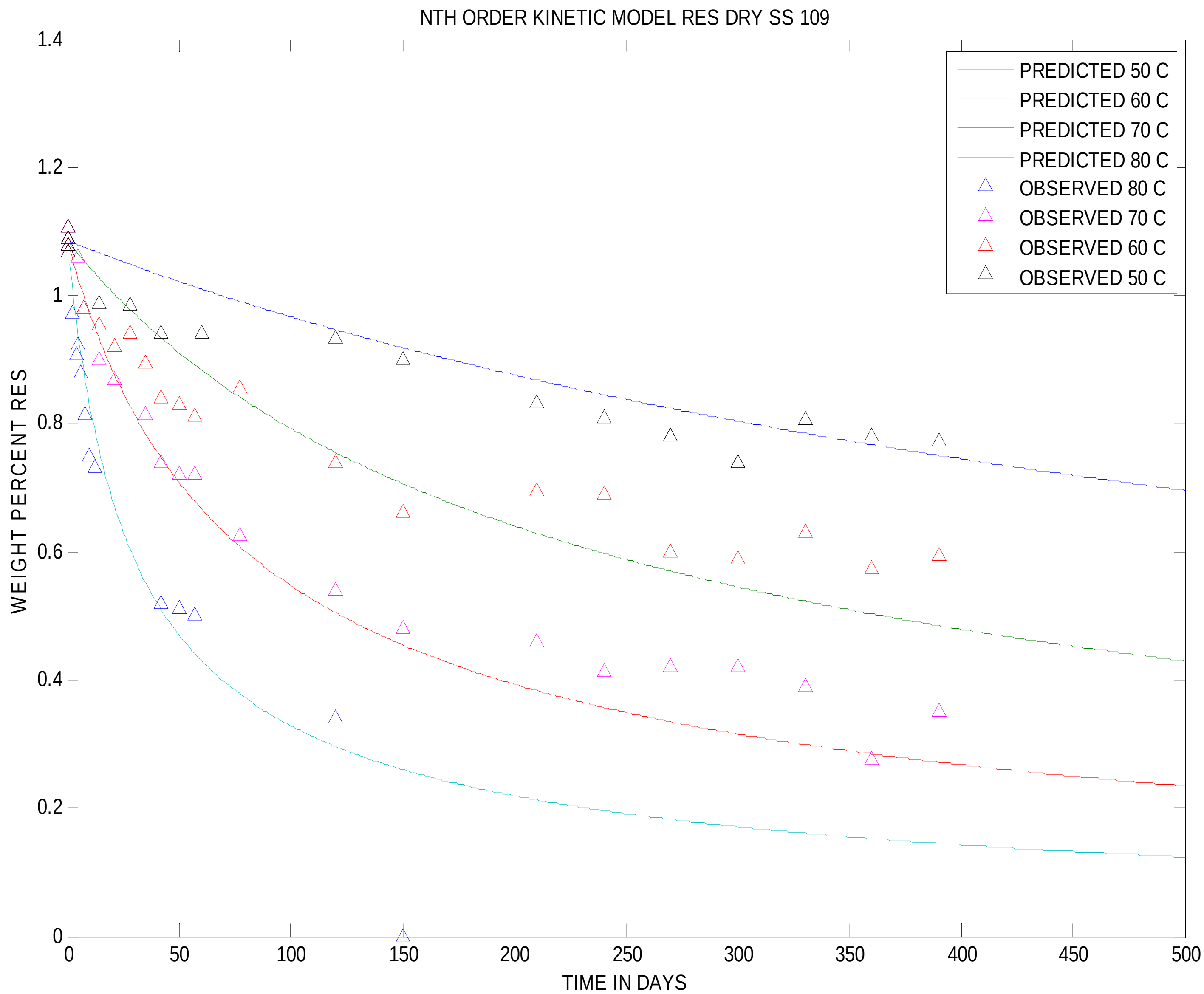


Figure 4: RES dry nth order



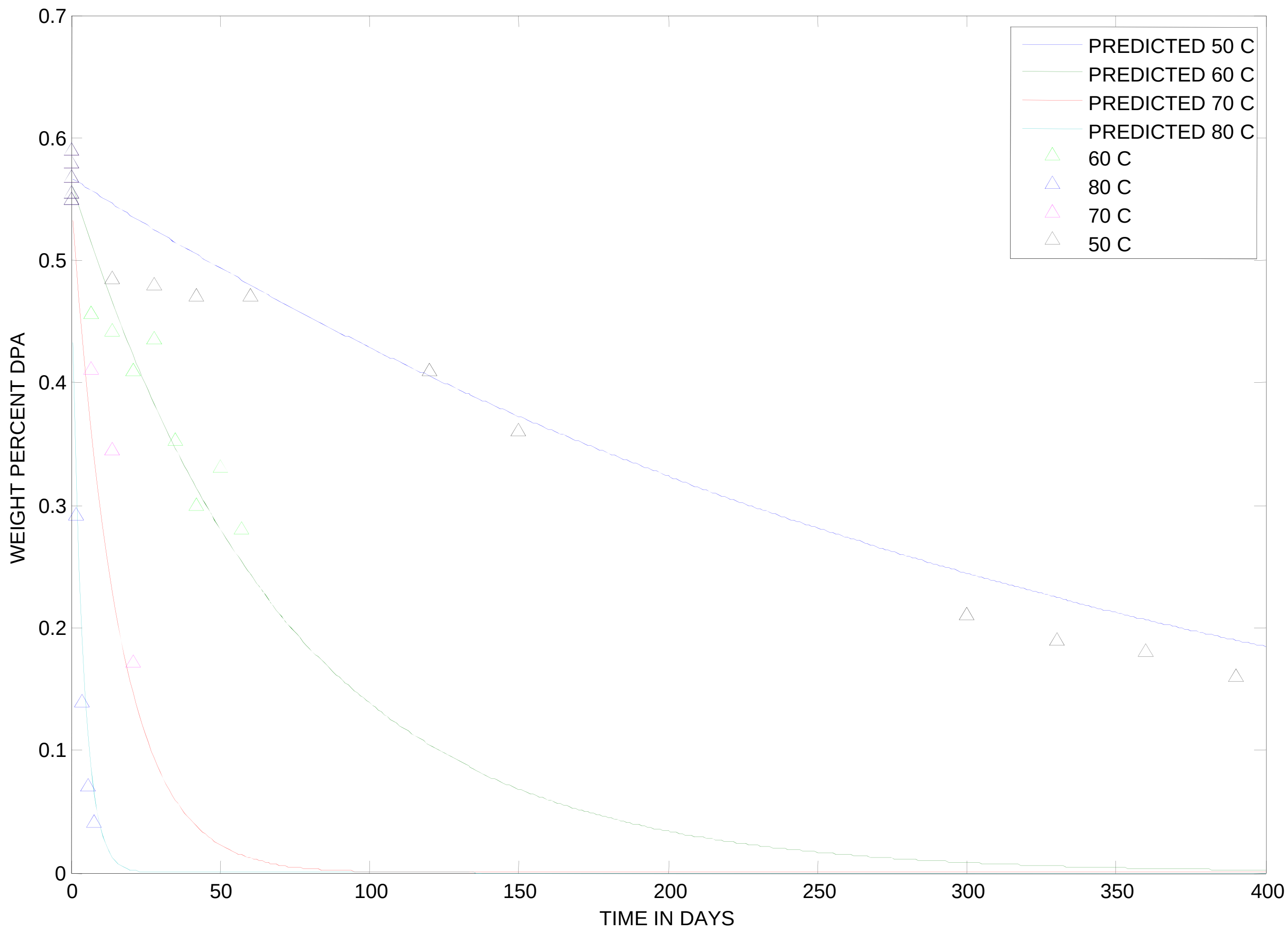


Figure 7. DPA dry first order

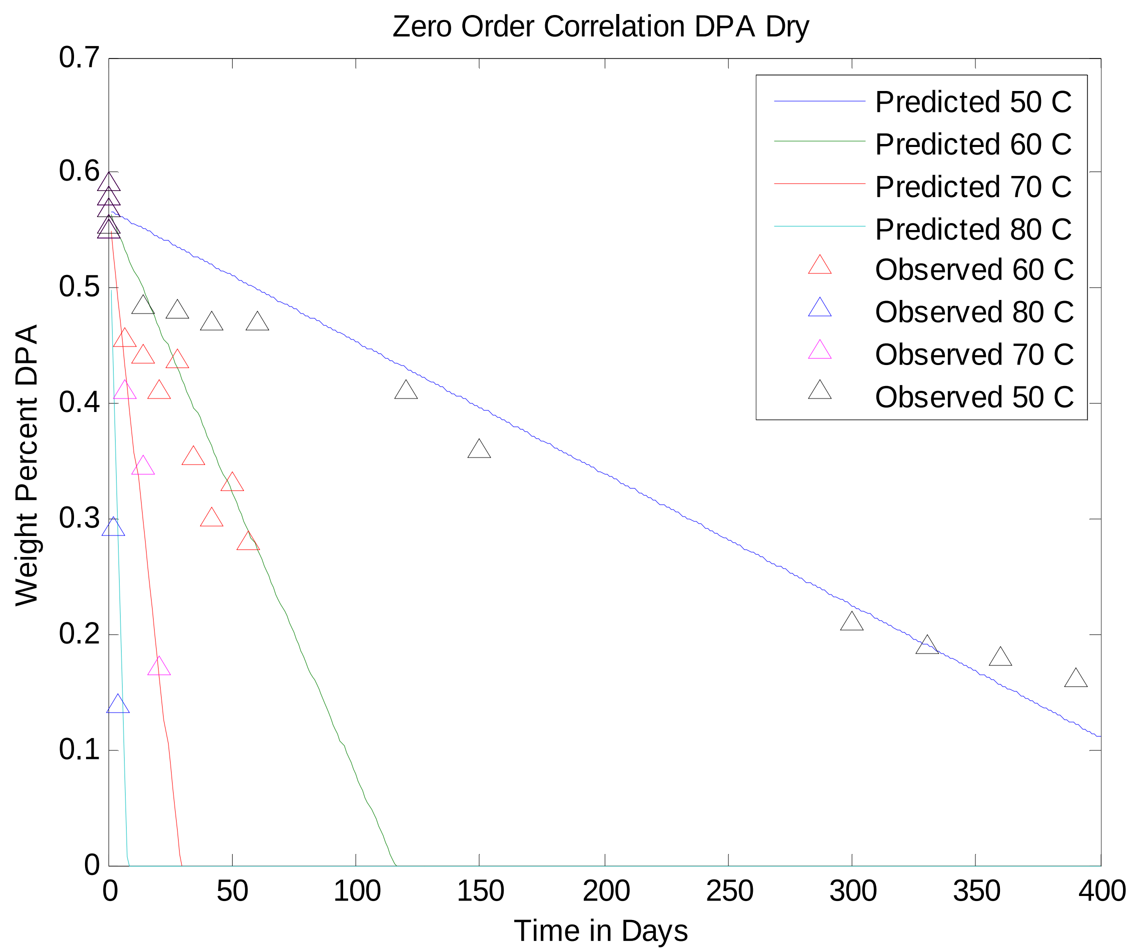


Figure 8 DPA dry zero order

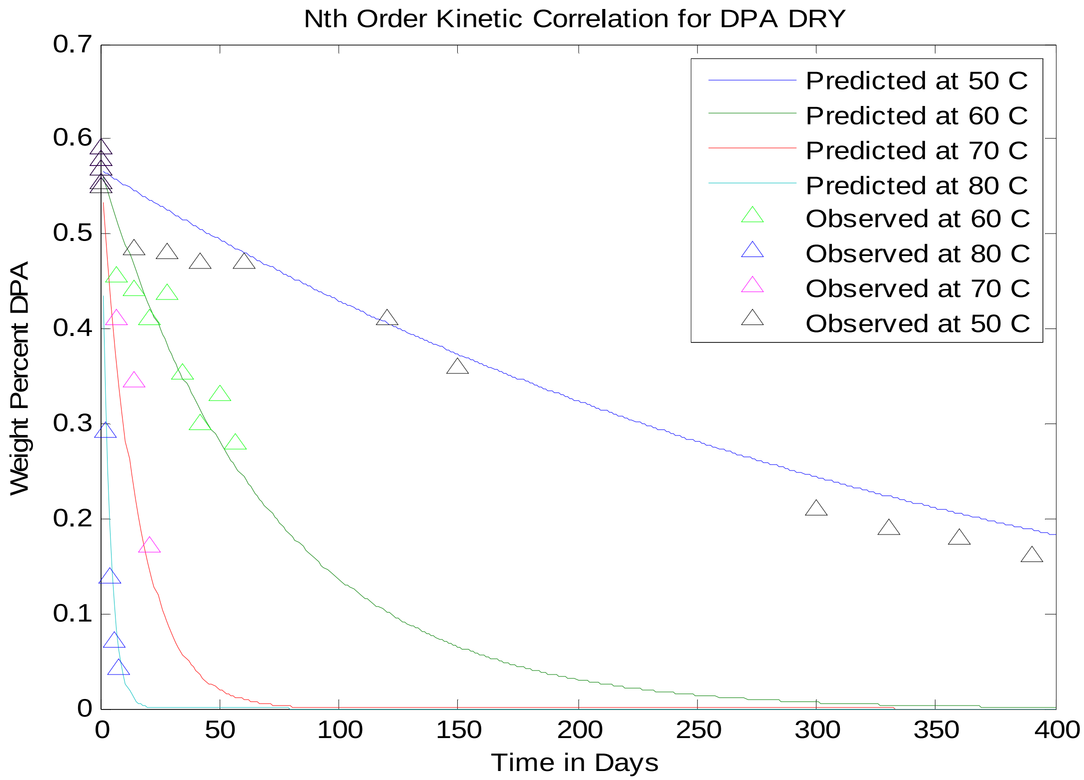
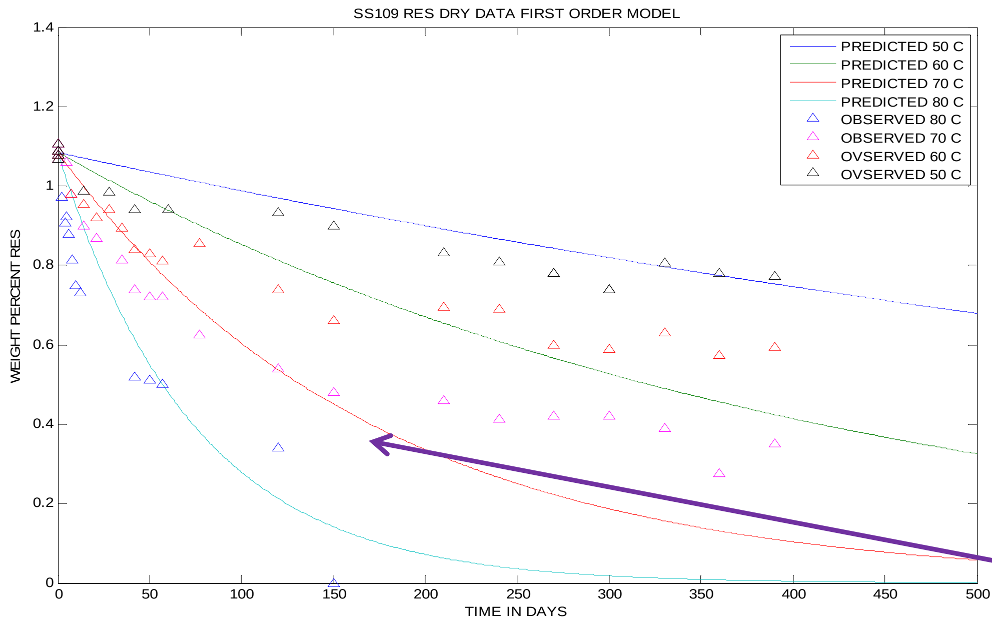
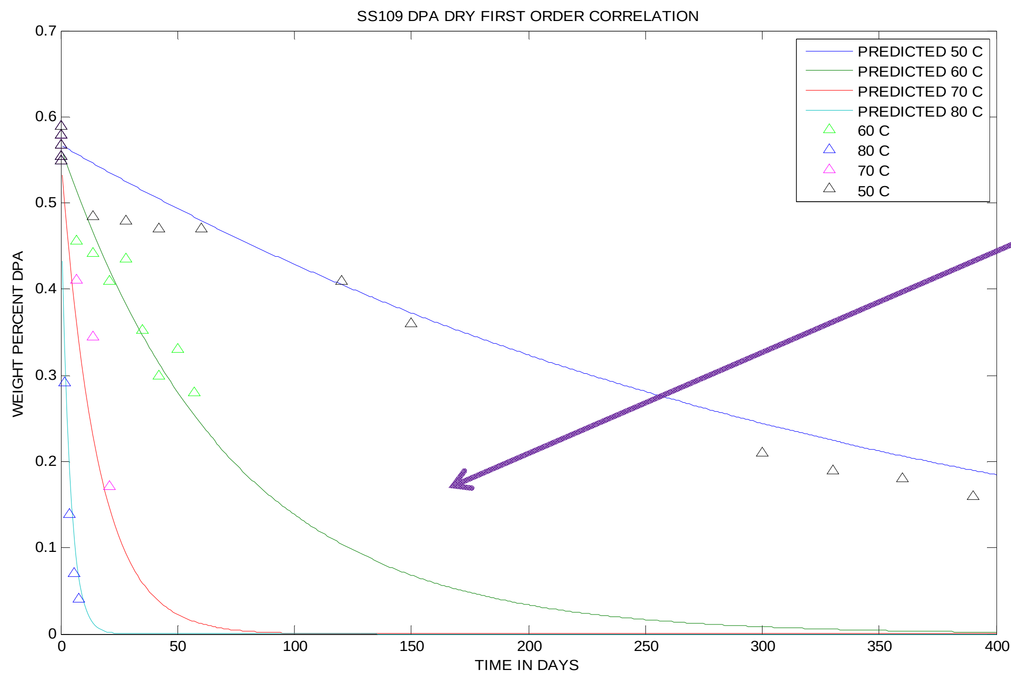


Figure 9 DPA dry Nth Order



RES DRY
DATA

High Temperature
Data (70 and 80)
clearly shows
RES lasts much longer
Than DPA



DPA DRY
DATA

Table IX. Modeling Results for diphenylamine (DPA)

Log 10 (Pre-exponential Factor)	Activation Temp (K)	MODEL	Residual Sum of Squares	Wet or Dry	Un-controlled Storage Life in Years	Controlled Storage Life in Years
19.481	7082.1	0th	.3660	Wet	.1306	77.0
18.9427	6774.9	1st	.0934	Wet	.0798	32.3
20.4226	7068.51	nth n=1.9771	.0929	Wet	.0590	34.3
18.102	6800.72	0th	.1054	Dry	.2336	102.9
20.798	7545.6	1st	.0481	Dry	.2090	199.8
20.7385	7530.63	nth n=2.500	.0482	Dry	.2089	196.6

Table VIII. Modeling Results For the Remaining Effective Stabilizer (RES)

Log 10 (Pre-exponential Factor)	Activation Temp (K)	MODEL	Residual Sum of Squares	Wet or Dry	Un-controlled Storage Life in Years	Controlled Storage Life in Years
9.1458	3943.2	0th	.7929	Wet	1.7346	43.6
11.4213	4638.6	1st	.4848	Wet	2.0675	102.0
13.3285	5250.2	nth n=1.755	.4579	Wet	1.7553	287.8
6.9392	3230.5	0th	1.6709	Dry	2.0582	26.5
10.6464	4419.3	1st	.7718	Dry	2.7429	109.1
13.7954	5411.9	nth n=2.500	.2760	Dry	6.97	742

Note that in this work, the remaining effective stabilizer includes all daughter products which are present at the time the sample is analyzed.

It is clear from the figures that the RES lasts much longer than the pure DPA.

RES = ∑ All DPA daughter products
Expressed as wt% equivalent DPA.

Future Work

- In the definition of RES used in this work, the reactivity of the highly nitrated daughter products is weighted the same as fresh DPA.
- This is not the case.
- Additional modeling needs to be done to estimate the relative rates of reaction for the daughter products of DPA

Summary

- Reaction Kinetic Models have been used to correlate the degradation data in a commercial ball powder.
- Estimates have been provided from three different models
- The results indicate that the DPA estimates are shorter than 2 years for the uncontrolled storage requirement. This is typical for DPA stabilized powders.

Summary

- When the lifetime is based on RES (which accounts for the DPA daughter products), the lifetime estimates are much longer, and the uncontrolled storage requirements are easily met for all the models based on the dry condition.
- The algorithm used to compute the effectiveness of the daughter products should be developed based on actual kinetic data rather than assuming that all the daughter products are stabilizers which are as effective as DPA.